Problem Set 5

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1) 10.22

	even	odd			even				
n	3	3	3	3	3	3	3	3	3
ℓ	0	1	1	1	2	2	2	2	2
m	0	0	-1	1	0	-2	-1	1	2

To be nonzero, $m' = m$ and the parity must be different.

$$H' = e\varepsilon r\cos\theta \tag{1}$$

Nonzero integrals:

$$\begin{aligned} &\langle 300|H'|300\rangle \\ &\langle 311|H'|321\rangle = \langle 31\text{-}1|H'|32\text{-}1\rangle \\ &\langle 310|H'|320\rangle \end{aligned} \tag{2}$$

We will do each one methodically (as they are very long).

$$\langle 300|H'|310\rangle \tag{3}$$

$$\begin{aligned} \psi_{300} &= \frac{1}{(3a_0)^{\frac{3}{2}}}\frac{1}{\sqrt{4\pi}}\left(2 - \frac{4r}{3a_0} + \frac{4r^2}{27a_0}\right)e^{-r/(3a_0)} \\ \psi_{310} &= \frac{1}{(3a_0)^{\frac{3}{2}}}\frac{4\sqrt{2}r}{9a_0}\left(1 - \frac{r}{6a_0}\right)e^{-r/(3a_0)}\sqrt{\frac{3}{4\pi}}\cos\theta \end{aligned} \tag{4}$$

$$\begin{aligned} &e\varepsilon\frac{1}{(3a_0)^2}\frac{4\sqrt{2}}{9a_0}\sqrt{\frac{3}{4\pi}}\underbrace{\int_0^{2\pi}\mathrm{d}\phi}_{2\pi}\underbrace{\int_0^{\pi}\cos^2\theta\sin\theta\,\mathrm{d}\theta}_{\frac{2}{3}}\underbrace{\int_0^{\infty} r\left(1 - \frac{r}{6a_0}\right)r^3 e^{2r/(3a_0)}\,\mathrm{d}r}_{-\frac{2187}{4}a_0^5} \\ &= -3\sqrt{6}e\varepsilon a_0 \end{aligned} \tag{5}$$

$$\langle 310|H'|320\rangle \tag{6}$$

$$\begin{aligned} \psi_{310} &= \frac{1}{(3a_0)^{\frac{3}{2}}}\frac{4\sqrt{2}r}{9a_0}\left(1 - \frac{r}{6a_0}\right)e^{-r/(3a_0)}\sqrt{\frac{3}{4\pi}}\cos\theta \\ \psi_{320} &= \frac{1}{(3a_0)^{\frac{3}{2}}}\frac{2\sqrt{2}r^2}{27\sqrt{5}a_0^2}e^{-r/(3a_0)}\sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \end{aligned} \tag{7}$$

$$\frac{1}{27a_0^3}\frac{2\sqrt{2}}{27\sqrt{5}a_0^2}\sqrt{\frac{5}{16\pi}}\frac{4\sqrt{2}}{9a_0}\sqrt{\frac{3}{4\pi}}\underbrace{\int_0^{2\pi}\phi}_{2\pi}\underbrace{\int_0^{\pi}\cos^2\theta\sin\theta(3\cos^2\theta-1)\,\mathrm{d}\theta}_{\frac{8}{15}}\underbrace{\int_0^{\infty}r^6\left(1-\frac{r}{6a_0}e^{-\frac{2r}{3a_0}}\,\mathrm{d}r\right)}_{-\frac{295245}{32}a_0^7} \tag{8}$$

$$= -3\sqrt{6}e\varepsilon a_0$$

$$\langle 311|H'|321\rangle \tag{9}$$

$$\begin{aligned}
\psi_{311} &= \frac{1}{(3a_0)^{\frac{3}{2}}}\frac{4\sqrt{2}r}{9a_0}\left(1-\frac{r}{6a_0}\right)e^{-r/(3a_0)}\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} \\
\psi_{321} &= \frac{1}{(3a_0)^{\frac{3}{2}}}\frac{2\sqrt{2}r^2}{27\sqrt{5}a_0^2}e^{-r/(3a_0)}\sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta e^{i\phi}
\end{aligned} \tag{10}$$

$$\frac{1}{27a_0^3}\sqrt{\frac{45}{64\pi^2}}\frac{8\cdot 2}{26\cdot 9\sqrt{5}}\frac{1}{a_0^3}\underbrace{\int_0^{2\pi}e^{i\phi-i\phi}\,\mathrm{d}\phi}_{2\pi}\underbrace{\int_0^{\pi}\sin^3\theta\cos^2\theta\,\mathrm{d}\theta}_{\frac{4}{15}}\underbrace{\int_0^{\infty}e^{-2r/(3a_0)}r^6\left(1-\frac{r}{6a_0}\right)\mathrm{d}r}_{-\frac{295245}{32}a_0^7} \tag{11}$$

$$= -\frac{9}{2}a_0 e\varepsilon$$

Now that we have the three integrals, we can create a matrix to hold the expectation values. We will also take out the factor of $-3a_0e\varepsilon$ in each term.

$$\begin{array}{cccccccccc}
 & 300 & 310 & 320 & 311 & 321 & 31\text{-}1 & 32\text{-}1 & 32\text{-}2 & 322 \\
300 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
310 & \sqrt{6} & 0 & \sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 \\
320 & 0 & \sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
311 & 0 & 0 & 0 & 0 & \frac{3}{2} & 0 & 0 & 0 & 0 \\
321 & 0 & 0 & 0 & \frac{3}{2} & 0 & 0 & 0 & 0 & 0 \\
31\text{-}1 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{3}{2} & 0 & 0 \\
32\text{-}1 & 0 & 0 & 0 & 0 & 0 & \frac{3}{2} & 0 & 0 & 0 \\
32\text{-}2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
322 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array} \tag{12}$$

As we can see, there are 3 (although 2 unique) submatrices that we can diagonalize to get the eigenvalues for the 9 degenerate states.

Let’s first do the 3x3 matrix.

$$\begin{aligned}
0 &= \begin{vmatrix} -\lambda & -a_0 e\varepsilon 3\sqrt{6} & 0 \\ -a_0 e\varepsilon 3\sqrt{6} & -\lambda & -a_0 3\varepsilon 3\sqrt{3} \\ 0 & -a_0 e\varepsilon 3\sqrt{3} & -\lambda \end{vmatrix} \\
&= -\lambda(\lambda^2 - a_0^2 e^2 \varepsilon^2 27) + a_0 e\varepsilon 3\sqrt{6}\left(\lambda e\varepsilon 3\sqrt{6}\right) \\
&= -\lambda^3 + \lambda a_0^2 e^2 \varepsilon^2 27 + \lambda a_0^2 e^2 \varepsilon^2 54 \\
&= -\lambda\left(\lambda^2 - (a_0 e\varepsilon 9)^2\right)
\end{aligned} \tag{13}$$

Hence $\lambda = 0, \pm 9ea_0\varepsilon$. Now we can find the eigenvectors.

We will first do $\lambda = 0$.

We know that $a^2 + b^2 + c^2 = 1$ by normalization. We also know (by plugging in $\lambda = 0$) that $b = 0$ and $a\sqrt{6} + c\sqrt{3} = 0$, so $c = \sqrt{1 - a^2}$.

$$\begin{aligned}
a\sqrt{6} + \sqrt{1 - a^2}\sqrt{3} &= 0 \\
-a\sqrt{6} &= \sqrt{3 - 3a^2} \\
3 - 3a^2 &= -a\sqrt{6} \\
3 - 3a^2 &= a^2 6 \\
3 &= a^2(6 + 3) \\
a &= -\frac{1}{\sqrt{3}} \quad \text{choose minus here} \\
\implies \quad c &= \sqrt{\frac{2}{3}}
\end{aligned} \tag{14}$$

Hence $|1\rangle = -\frac{1}{\sqrt{3}}|300\rangle + \sqrt{\frac{2}{3}}|320\rangle$.

Now we can do $\lambda = 9ea_0\varepsilon$.

We can see (by row reducing) that $a = \sqrt{2}c, b = \sqrt{3}c$ and that $a^2 + b^2 + c^2 = 1$. We find that $a = \frac{1}{\sqrt{3}}, b = \frac{1}{\sqrt{2}}, c = \frac{1}{\sqrt{6}}$.
Hence $|2\rangle = \frac{1}{\sqrt{3}}|300\rangle + \frac{1}{\sqrt{2}}|310\rangle + \frac{1}{\sqrt{6}}|320\rangle$.

Now we do $\lambda = -9ea_0\varepsilon$.

From row reduction we see that $a = \sqrt{2}c, b = -\sqrt{3}c$ and normalization as above. We find that $a = \frac{1}{\sqrt{3}}, b = -\frac{1}{\sqrt{2}}, c = \frac{1}{\sqrt{6}}$.
Hence $|3\rangle = \frac{1}{\sqrt{3}}|300\rangle + -\frac{1}{\sqrt{2}}|310\rangle + \frac{1}{\sqrt{6}}|320\rangle$.

Now we look at the two other submatrices that look like this:

$$\begin{vmatrix} -\lambda & -\frac{9}{2}a_0 e\varepsilon \\ -\frac{9}{2}a_0 e\varepsilon & -\lambda \end{vmatrix} = 0 \tag{15}$$

Solving for λ gives us $\lambda = \pm\frac{9}{2}a_0 e\varepsilon$.

We can solve for the eigenvectors, and we can see that because it is a 2x2 matrix that is symmetric we will have coefficients of $\pm\frac{1}{\sqrt{2}}$ for each term.

Hence $|4\rangle = \frac{1}{\sqrt{2}}|311\rangle + \frac{1}{\sqrt{2}}|321\rangle, |5\rangle = \frac{1}{\sqrt{2}}|311\rangle - \frac{1}{\sqrt{2}} + |321\rangle$.

And using similar reasoning we can see that $|6\rangle = \frac{1}{\sqrt{2}}|31\text{-}1\rangle + \frac{1}{\sqrt{2}}|32\text{-}1\rangle, |7\rangle = \frac{1}{\sqrt{2}}|31\text{-}1\rangle - \frac{1}{\sqrt{2}}|32\text{-}1\rangle$.

Because the final two states do not have any nonzero values in their rows/columns, we know that $|8\rangle = |322\rangle, |9\rangle = |32\text{-}2\rangle$ (they do not change with the dipole).

Now we can see how the dipole moment changes with this electric field.

We know that the dipole moment $\vec{d} = -e\vec{r}$.

$$\begin{aligned} H' &= -\vec{d} \cdot \vec{E} \\ &= -d_z E_z = e\varepsilon r \cos\theta \\ \implies \quad d_z &= -\frac{e\varepsilon r \cos\theta}{E_z} \\ d_z &= -\frac{H'}{\varepsilon} \end{aligned} \tag{16}$$

So:

$$\langle nlm|d_z|n'l'm'\rangle = -\frac{1}{\varepsilon}\underbrace{\langle nlm|H'|n'l'm'\rangle}_{\text{new eigenvalues}} \tag{17}$$

So the change to the dipole moment is $\frac{1}{\varepsilon}E_n^{(1)}$.

For the changes to the energies that are zero, that means that the dipole is orthogonal with the magnetic field. For the others, they are all negative which means that it is aligned (because we have the -1 in d_z).

$$
\begin{aligned}
|1\rangle &= -\frac{1}{\sqrt{3}}|300\rangle + \sqrt{\frac{2}{3}}|320\rangle & \lambda &= 0 \\
|2\rangle &= \frac{1}{\sqrt{3}}|300\rangle + \frac{1}{\sqrt{2}}|310\rangle + \frac{1}{\sqrt{6}}|320\rangle & \lambda &= 9ea_0\varepsilon \\
|3\rangle &= \frac{1}{\sqrt{3}}|300\rangle + -\frac{1}{\sqrt{2}}|310\rangle + \frac{1}{\sqrt{6}}|320\rangle & \lambda &= -9ea_0\varepsilon \\
|4\rangle &= \frac{1}{\sqrt{2}}|311\rangle + \frac{1}{\sqrt{2}}|321\rangle & \lambda &= -\frac{9}{2}a_0e\varepsilon \\
|5\rangle &= \frac{1}{\sqrt{2}}|311\rangle - \frac{1}{\sqrt{2}} + |321\rangle & \lambda &= \frac{9}{2}a_0e\varepsilon \\
|6\rangle &= \frac{1}{\sqrt{2}}|31\text{-}1\rangle + \frac{1}{\sqrt{2}}|32\text{-}1\rangle & \lambda &= -\frac{9}{2}a_0e\varepsilon \\
|7\rangle &= \frac{1}{\sqrt{2}}|31\text{-}1\rangle - \frac{1}{\sqrt{2}}|32\text{-}1\rangle & \lambda &= \frac{9}{2}a_0e\varepsilon \\
|8\rangle &= |322\rangle & \lambda &= 0 \\
|9\rangle &= |32\text{-}2\rangle & \lambda &= 0
\end{aligned} \tag{18}
$$

The states that have negative eigenvalues (the perturbed energy) align with the dipole and the ones which have positive are anti-aligned. If the state has a 0 change to its energy, then it is orthogonal to the dipole.

This is because the eigenvalues correspond to $-\frac{1}{\varepsilon}$ of the dipole moment.